

Reconnaissance Stable Isotope (C, O, H, S) Study of Paleoproterozoic Gold Deposits of the São Luis Craton and Country Rocks, Northern Brazil: Implications for Gold Metallogeny

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Abstract

Caxias, Areal, and Pedra de Fogo are structurally controlled syn- to late tectonic and post-metamorphic gold deposits of Paleoproterozoic age located in the São Luis craton, northern Brazil. Previous fluid inclusion studies indicated reduced, low-salinity CO₂-H₂O (±CH₄-N₂) fluids trapped at 260°–300°C (Caxias, Areal) to 330°–400°C (Pedra de Fogo), and at 2 kbar as responsible for the mineralization. Oxygen isotope ratios of quartz (+10.4 to +16.2‰), chlorite (+7.6‰), and sericite (+5.1‰), and hydrogen isotope ratios of chlorite (–46‰), sericite (–58‰), and fluid inclusion water (–32 to –70‰) indicate fluid δ¹⁸O values of +2.6 to +5.6 per mil (Caxias), +0.6 to +3.5 per mil (Areal), and +10.3 to +12.1 per mil (Pedra de Fogo) and fluid δD composition of –24 to –53 per mil (Caxias), –49 to –62 per mil (Areal), and –70 per mil (Pedra de Fogo) at the assumed temperatures. These estimated fluid compositions are consistent with metamorphic sources. Calcite and fluid inclusion CO₂ δ¹³C values between –3.1 and –10.9 per mil are not diagnostic of a particular origin, but a more negative value (–20.2‰) found at Caxias indicates a greater organic component, at least locally. Sulfide δ³⁴S values of –2.8‰ to –11.0‰ reflect possible achievement of more oxidized conditions. Hydrogen and oxygen isotope analyses of the country rocks suggest minor isotope disequilibrium and resetting of oxygen isotope geothermometers. This might indicate subsolidus post-crystallization isotopic exchange, linked with metamorphism and/or hydrothermal alteration.

Introduction

THE SÃO LUIS CRATON in northern Brazil hosts several gold occurrences and small deposits. With the exception of the Aurizona deposit, which lies close to the Atlantic coast, most of the mineralized zones are located in the central portion of the craton (Figs. 1 and 2), a region where geological complexities, including lithologic variation, and density of ductile and brittle structures are more intense than elsewhere in the craton. Geological, chemical, and fluid

inclusion studies have been completed for the Caxias, Areal (Klein et al., 2000; Klein et al., 2002), and Pedra de Fogo (Klein and Fuzikawa, 2005) deposits. These studies constrained the main attributes of those deposits, including host rocks, hydrothermal alteration, structural control, and the physicochemical conditions (P-T-X-*f*O₂) of ore formation. However, the sources for the ore-bearing fluids and metals have not been fully addressed due to inherent limitations of the employed methodologies. In this paper we present stable isotope (C, O, H, S) data for minerals from the hydrothermal assemblage of these three prospects, and also for

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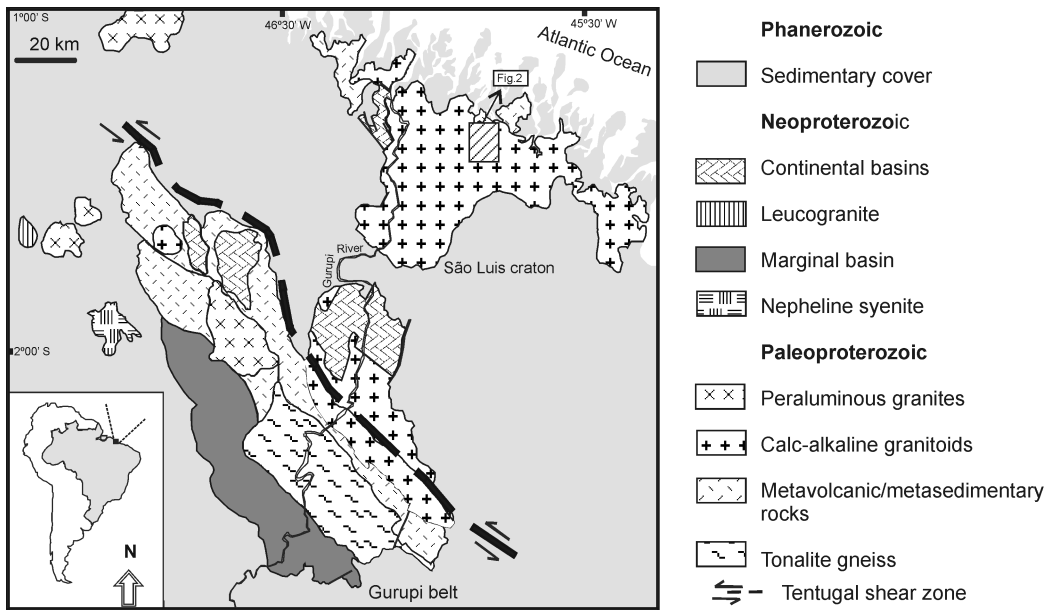


FIG. 1. Geological map of the São Luís craton.

regional and gold-hosting rocks of the São Luís craton at a reconnaissance scale. This study, integrated with previously available information, allows us to improve knowledge about the genesis of gold mineralization in the craton.

Geological Overview

The São Luís craton comprises a few suites of granitoids, a metavolcanosedimentary succession, and subordinate volcanic rocks, which are covered by younger sedimentary basin deposits (Fig. 1). The metavolcanosedimentary sequence (Aurizona Group) is composed of schists, metavolcanic and metapyroclastic rocks, along with subordinate quartzite, metachert, and metamafic-ultramafic rocks (Pastana, 1995). These rocks show greenschist-facies metamorphic paragenesis, and locally attained the lower amphibolite facies. They also show a regional schistosity that strikes N15°–70°W, and dips steeply (>70°) to the northeast. A metapyroclastic rock that hosts gold mineralization in the Pedra de Fogo prospect has been dated by Pb evaporation in zircon, yielding an age of 2240 ± 5 Ma (Klein and Moura, 2001), interpreted as being an early volcanic event in the evolutionary history of the craton.

The Tromaf Intrusive Suite is the largest unit in the area (Fig. 1), consisting of batholiths of tonalite and subordinate trondhjemite, granodiorite, and monzogranite. These rocks show variable textural and structural aspects, being porphyritic to equigranular, foliated to massive, and contain centimeter- to meter-scale microgranular enclaves of mafic to intermediate composition. The igneous mineralogy and textures are well preserved despite late hydrothermal/metamorphic overprinting, recorded by saussuritization of plagioclase, and chloritization of biotite and amphibole. They are metaluminous, sodic, calc-alkaline rocks. Single zircon Pb evaporation ages range between 2149 ± 5 Ma and 2165 ± 2 Ma (Klein and Moura, 2001).

Dacite and rhyodacite occur as isolated blocks, mostly without visible contact relationships, and locally as dikes that cut across the granitoids. They are unmetamorphosed and generally undeformed, showing preserved volcanic structures and textures. No geochronological data are available for these rocks.

The Areal Granite is the host for the mineralization of the Areal prospect, and is composed of chemically evolved, K-rich calc-alkaline granites that are restricted to a single stock cropping out in the north-central portion of the craton (Figs. 1 and 2). The

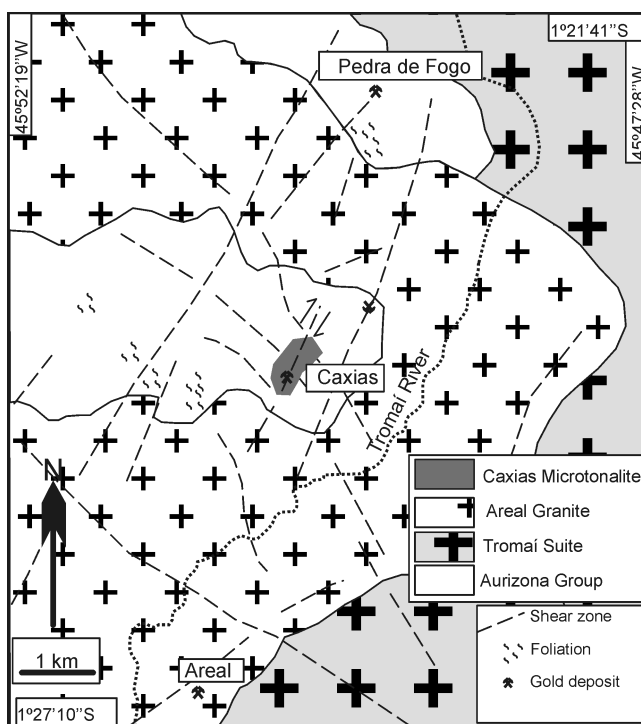


FIG. 2. Geological map of the central portion of the São Luís craton, showing locations of the Caxias, Areal, and Pedra de Fogo gold deposits (adapted from Klein et al., 2002).

granites are porphyritic to equigranular and do not show tectonic deformation, except along discrete (cm-wide) brittle-ductile shear zones, or in the contacts with the metavolcanosedimentary rocks. They contain large enclaves of supracrustal rocks, possibly related to the Aurizona Group in which they were intruded. Pb evaporation zircon ages are in the range of 2149–2152 Ma (Klein and Moura, 2003).

Peraluminous, muscovite-bearing granitoids crop out in the northwestern portion of the area (Fig. 1). These granitoids were grouped in the Tracuateua Intrusive Suite by Costa (2000), and have a Pb evaporation zircon age of 2090 Ma (Palheta, 2001). This suite is similar to granitoids that occur in the Gurupi belt, which borders the SSW margin of the craton and is considered to represent collision-type granitoids related to the final phase of the Paleoproterozoic (Transamazonian/Eburnean) accretionary-collisional orogen (Klein and Moura, 2001, 2003).

The Caxias microtonalite is a small body that intruded the schists of the Aurizona Group and hosts the gold mineralization in the Caxias deposit. It is an equigranular, isotropic to foliated rock (where cut

by shear zones), showing strong effects of hydrothermal alteration. Klein et al. (2002) determined an age of 1985 Ma for the intrusion (single zircon Pb evaporation).

In the central portion of the craton, where the gold deposits studied here are located (Figs. 1 and 2), structures strike predominantly NNE-SSW and WNW-ESE. The structures are mostly discrete shear zones, up to a few hundred meters wide and a few km long, that crosscut both the granitoids and the supracrustal rocks. These discrete shear zones are economically important because they host most, if not all, the known gold mineralization in the cratonic area.

Collectively, the available geological, petrologic, and geochronological information points to an orogenic evolution for the São Luís craton occurring between 2240 and 2000 Ma, with the main calc-alkaline magmatism taking place in a shorter time interval, between 2165 and 2148 Ma. This is likely related to the evolution of magmatic arcs during the accretionary part of the Paleoproterozoic orogen that culminated with collisional activity at 2100–2080

Ma (Palheta, 2001; Klein and Moura, 2001, 2003). This evolution exhibits strong similarities to that of the Paleoproterozoic domain of the West African craton (e.g., Doumbia et al., 1998; Hirdes and Davis, 2002) and reinforces previous correlations in which the São Luis craton is regarded as a small fragment of the West African craton that was left behind after the breakup of the Pangea supercontinent (Lesquer et al., 1984; Ledru et al., 1994).

The age of gold mineralization in the cratonic area is not fully constrained. An upper limit of 1985 Ma is placed at least for the Caxias deposit, which is the crystallization age of the host microtonalite. A lower limit is established by available Rb-Sr and K-Ar data on minerals and whole rocks (see Klein and Moura, 2001, 2003 for primary references), which show that the rocks were not affected by any thermal event after about 1900 Ma. Accordingly, the gold mineralization occurred late in the evolution of the São Luis craton, having post-metamorphic and syn- to late-tectonic characteristics (see below).

Summary of Geological and Fluid Inclusion Data

Caxias

In the Caxias deposit, the host rocks are the Caxias Microtonalite and schists of mafic and pelitic composition that belong to the Aurizona Group. Mineralization was controlled by a ductile-brittle shear zone that strikes N15°E and dips 75° to the SE. Hydrothermal alteration produced widespread quartz veining, pervasive chloritization and sulfidation, along with minor amounts of sericitization and carbonatization. The veinlets are continuous to disrupted and a few millimeters to centimeters thick, and they reach several tens of meters along strike. Quartz from these veinlets shows a milky, massive to saccharoidal aspect. Chlorite is widespread, both in the microtonalite and in the schists. Pyrite is the predominant sulfide mineral, with subordinate amounts of sphalerite occurring in the northern sector of the deposit (microtonalite-hosted). Magnetite occurs as a subordinate phase in the southern sector (schist-hosted). Gold occurs in the free state in the contact between chlorite and quartz grains or associated with sulfides. Gold contents are highly variable, grading mainly 3 to 369 ppb, and locally attaining 590–3000 ppb. Arsenic and Sb are invariably present, but they show generally low values, whereas high Ni, Co, V, and Cr values are associated

with higher concentrations of Au and As (Klein et al., 2002).

Detailed fluid inclusion study (Klein et al., 2000) characterized a CO₂ (±N₂)-H₂O-NaCl ore-bearing fluid having moderate bulk density (0.7 to 1.0 g/cm³), average salinity of 5 wt% NaCl equiv., and containing 6–45 mol% of CO₂ and up to 2.5 mol% of N₂. Subordinate amounts of CH₄ occur in the southern sector of the deposit (schist-hosted) and are interpreted as reflecting contamination of the fluid by carbon-bearing host rocks at the site of gold deposition. Homogenization temperatures, combined with chlorite geothermometry (Klein and Koppe, 2000) bracket ore formation at 262°–307°C and 1.6 to 3.7 kbar, implying depths of 5–15 km (brittle-ductile transition). Mineralogical and fluid characteristics indicate relatively reduced conditions (log *f*O₂ between -34 and -30) and transport of gold by a reduced sulfur complex, probably AuHS₂⁻. Gold deposition has been interpreted as occurring in response to a combination of phase separation, reduction of the H₂S activity, and lowering of *f*O₂ due to fluid-rock interactions.

Areal

Gold mineralization in the Areal prospect occurred in sets of moderate to steeply dipping, centimeter- to decimeter-thick, tabular milky quartz veins, which fill brittle structures that crosscut the Areal Granite. The veins strike dominantly to N45°W and N20°E, and are surrounded by narrow haloes of sericitic alteration. Fine-grained sericite occurs in high proportions in the narrow hydrothermal haloes and in minor amounts in the distal portions of the altered host rock. Pyrite is distributed in the sharp contacts between the veins and the altered wall rock. Pyrite is euhedral and coarse-grained near the veins, and forms disseminations and aggregates of fine-grained crystals in the distal portions. Magnetite is highly subordinate. Enrichments of As, Sb, Mo, and Br have been detected and are suggested as the most prospective elements, in addition to gold that grades generally lower than 200 ppb (Klein, 1998).

Fluid inclusion study (Klein et al., 2000) revealed that physicochemical conditions at Areal were remarkably similar to those of the Caxias deposit (Table 1). The fluids have nearly identical compositions and densities, and the homogenization temperatures are mainly in the range of 260° to 300°C. Trapping pressures have been estimated between 1.3 and 3.5 kbar. The same interpretations

TABLE 1. Geological and Physicochemical Properties of Gold Mineralization in the Caxias, Areal, and Pedra de Fogo Gold Deposits

Property	Caxias	Areal	Pedra de Fogo
Host rock	Microtonalite	Monzogranite	Metapyroclastic
Host structure	Ductile-brittle shear zone	Faults/fractures	Fracture
Structural style	Veinlets / dissemination	Quartz veins	Quartz veins
Alteration assemblage ¹	qz, cc, chl, ser, py, (sph)	qz, ser, py	qz, chl, ser, py, (cpy)
Metal association	Au, As, Sb, Ni, Co, V, Cr	Au, As, Sb, Mo, Br	Au, As ²
Gold grade	3 to 369 ppb	<200 ppb	<281 ppb ²
Fluid composition	CO ₂ -(N ₂ -CH ₄)-H ₂ O-NaCl	CO ₂ -(N ₂)-H ₂ O-NaCl	CH ₄ -(N ₂)-H ₂ O-NaCl/CO ₂ -H ₂ O-NaCl
XCO ₂ / XCH ₄ / XN ₂	0.6–0.45/tr ³ / <2.5	0.05–0.2 /tr/ <2	n.d. ⁴
Wt% NaCl equiv.	5	5	<15
Bulk density (g/cm ³)	0.7 to 1.0	0.8 to 1.0	~0.7
T (°C)	262 to 307	260 to 300	330 to 400
P (kbar)	1.6 to 3.7	1.3 to 3.5	2
log <i>f</i> O ₂	–34 to –30	–35 to –31	n.d.

¹ qz = quartz, cc = calcite; chl = chlorite; ser = sericite; py = pyrite, sph = sphalerite; cpy = chalcopyrite.

² Unpublished data.

³tr = traces.

⁴n.d. = not determined.

concerning the transport and deposition of gold at Caxias are valid here.

Pedra de Fogo

Pedra de Fogo is a small occurrence hosted in brittle structures that cut across a metapyroclastic rock belonging to the metavolcanosedimentary Aurizona Group. Mineralization formed 20 to 50 cm thick milky quartz veins that nearly lack hydrothermal haloes. Veins are subvertical, strike N45°W, and cut across the regional foliation, being clearly postmetamorphic (Klein and Fuzikawa, 2005). Except for the host rock, the structural style is quite similar to that of the Areal prospect. In distal portions of the deposit, altered metadacites contain chlorite and small amounts of sericite and epidote, in addition to discordant layers and disseminations of pyrite, rare chalcopyrite, and magnetite.

The fluid inclusion and chlorite chemistry studies carried out by Klein and Fuzikawa (2005) reveal rather distinct physicochemical characteristics for

Pedra de Fogo compared to the results for the Caxias and Areal deposits (Table 1). The results are interpreted as reflecting the trapping of an evolving aqueous-carbonic fluid. This fluid was initially hotter (>430°C) and reduced, as depicted by CH₄-H₂O inclusions that lack CO₂. Under cooling and more oxidized conditions, CO₂ became the carbonic species in the aqueous-carbonic fluid. This fluid has salinities lower than 15 wt% NaCl equiv., and was trapped mostly between 330°–400°C at about 2 kbar. The lower temperature limit is coincident with the equilibrium temperature of the hydrothermal chlorites.

Analytical Procedures

Carbon, oxygen, and hydrogen isotope analyses were performed at the Laboratoire des Isotopes Stables of the Université Jean Monnet, Saint Etienne, France. Sulfur isotopes were analyzed at the Stable Isotope and ICP/MS laboratory of Queen's

University, Kingston, Ontario, Canada. Carbon dioxide was released from calcite by reaction with 100% H_3PO_4 (McCrea, 1950). For oxygen analysis, the conventional fluorination method (Clayton and Mayeda, 1963) was employed for whole rocks and hydrous minerals, and a CO_2 laser fluorination system (Harris et al., 2000) was used for quartz analysis. In both systems, oxygen was produced by reacting the samples with BrF_5 and then converted to CO_2 by reaction with graphite. Hydrogen was produced by heating the mineral concentrates in vacuum, following procedures described in Venne-mann and O'Neil (1993). The extracted H_2 was first converted to H_2O by passing through a CuO furnace heated at $\sim 600^\circ\text{C}$ and purified cryogenically, then reduced to H_2 by reaction with zinc in vacuum at 450°C , according to procedures adapted from Coleman et al. (1982). Inclusion fluids were extracted from ~ 1 – 2 g of degassed quartz by thermal decrepitation in an evacuated quartz tube heated at $>800^\circ\text{C}$. Both CO_2 and H_2O were recovered. Hydrogen conversion followed the same procedures described for the hydrous minerals, and CO_2 was isolated with a cold trap. For sulfur analysis, SO_2 was produced from sulfide minerals loaded into tin capsules and reacted with CuO at 1400°C in a He stream. The analytical uncertainties are 0.3‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, 4‰ for δD , and 0.5‰ for $\delta^{34}\text{S}$. The isotope ratios are all reported in the delta (per mil) notation, relative to the PDB (C), SMOW (O and H), and CDT (S) scales.

Stable Isotope Geochemistry of Regional Rocks

Results

Oxygen and hydrogen isotope compositions have been determined for whole rocks and silicate mineral samples from the Tromaf Intrusive Suite, Areal Granite, Caxias Microtonalite, and Aurizona Group. The results are presented in Table 2 and displayed graphically in Figure 3.

For the granitoids of the Tromaf Intrusive Suite, the $\delta^{18}\text{O}$ values of whole rocks and magmatic quartz range between +8.5 and +9.9‰, and between +9.8 and +11.2‰, respectively. Amphibole and biotite have $\delta^{18}\text{O}$ values in the range of +4.0 and +8.7‰. The δD values of the whole rocks and hydrous silicates lie between -26 and -62 ‰. The quartz, whole rocks, and biotite of the Areal Granite show $\delta^{18}\text{O}$ values of +6.6 to +10.0‰, +5.9 to +9.6‰, and +2.7

to 3.1‰, respectively. The whole-rock and biotite δD values range from -41 to -68 ‰. In the Caxias Microtonalite, $\delta^{18}\text{O}$ and δD values of whole rocks are respectively +11.2 and -48 ‰ in the least altered sample, and +10.6 and -46 ‰ in the strongly hydrothermally altered sample. The quartz in these two samples shows $\delta^{18}\text{O}$ values of +9.8 and +12.7‰, respectively. One sample of hydrothermally altered metadacite belonging to the Aurizona Group has $\delta^{18}\text{O}$ and δD values of +18.7 and -51 ‰, respectively.

Discussion

The overall isotopic values obtained from the granitoid rocks are considered as normal for these types of rocks (Taylor and Sheppard, 1986), with the exception of the rather high δD value of amphibole in sample EK2 of the Tromaf Suite (-26 ‰). The metadacite (PF1A) shows an abnormally high $\delta^{18}\text{O}$ value that may be ascribed to low-temperature hydrothermal alteration.

Estimations of the isotope composition of the magmas of the Tromaf and Areal granitoids have been made according to the approach adopted by Harris et al. (1997), using the oxygen isotope composition of quartz and the hydrogen isotope composition of biotite. The Tromaf Suite shows $\delta^{18}\text{O}$ values of +7.8 to +8.3‰, and δD values of -32 to -28 ‰. The Areal Granite has rather high $\delta^{18}\text{O}$ values ranging from +4.6 to +8.0‰, and δD values in the interval of -38 to -33 ‰. However, applying the quartz-biotite oxygen geothermometer and fractionation factor of Bottinga and Javoy (1975), temperatures between 430° and 630°C have been obtained. Considering the temperatures of the solidus for calc-alkaline granitic systems ($\sim 630^\circ\text{C}$; Carroll and Wyllie, 1990), and the temperature of closure of the minerals to oxygen diffusion ($\sim 550^\circ\text{C}$; Gilletti, 1986), it appears that the mineral-pair fractionations have been at least partially reset to low temperatures. Furthermore, despite the small number of analysis, the δ - δ diagrams of Figure 3 more likely indicate some isotope exchange/re-equilibration at subsolidus conditions (e.g., Gregory and Criss, 1986; Taylor and Sheppard, 1986; Harris et al., 1997), which is in keeping with the petrographic evidence that shows saussuritization of plagioclase and chloritization of biotite and amphibole. Therefore, inasmuch as quartz is not very vulnerable to post-crystallization effects, it likely records its original magmatic isotope composition, and the above temperatures are probably meaningless.

TABLE 2. Oxygen and Hydrogen Isotope Composition of Minerals and Whole Rocks from Country Rocks of the São Luís Craton

Sample	Rock type	Material	$\delta^{18}\text{O}$ (‰)	δD (‰)
Tromaf Suite				
EK2	Trondhjemitite	WR	9.9	-32
EK2	Trondhjemitite	Quartz	12.7	
EK2	Trondhjemitite	Amphibole	6.8	-26
EK3A	Monzogranite	WR	8.5	-52
EK3A	Monzogranite	Quartz	9.8	
EK3A	Monzogranite	Biotite	4.0	-62
EK5A	Tonalite	WR	9.6	-44
EK5A	Tonalite	Quartz	10.3	
EK5A	Tonalite	Biotite	6.4	-58
EK5A	Tonalite	Amphibole	8.7	-53
Areal Granite				
EK4	Monzogranite	WR	7.8	-41
EK4	Monzogranite	Quartz	10.0	
EK4	Monzogranite	Biotite	3.1	-68
EK7	Syenogranite	WR	5.9	-51
EK7	Syenogranite	Quartz	6.6	
EK7	Syenogranite	Biotite	2.7	-63
AR10C	Syenogranite	WR	9.6	-49
Caxias Microtonalite				
CX65	Microtonalite	WR	10.6	-46
CX65	Microtonalite	Quartz	12.7	
CX47	Microtonalite	WR	11.2	-48
CX47	Microtonalite	Quartz	9.8	
Aurizona Group				
PF1A	Metadacite	WR	18.7	-51

Stable Isotope Geochemistry of the Gold Deposits

Results

The analyzed quartz samples come from veins and veinlets, whereas chlorite and sericite were separated from the wall rock alteration. The isotope results are presented in Table 3. The $\delta^{18}\text{O}$ values of quartz from the Caxias deposit cluster tightly between +11.0 and +12.2‰. At Areal and Pedra de Fogo, the $\delta^{18}\text{O}$ value of quartz is +10.4 and +16.2‰, respectively. The oxygen isotope composition of the chlorite sample of the Caxias deposit is +7.6‰ and its δD is -46‰. The sericite sample of the Areal prospect shows a $\delta^{18}\text{O}$ value of +5.1‰

and δD of -58‰. The δ values of inclusion water ranges from -24 to -53‰ at Caxias, and are -62 and -70‰ in the Areal and Pedra de Fogo prospects, respectively. The variation in the δD values of inclusion waters at Caxias cannot be accounted for by mixing between waters of different isotope composition, given the uniformity of the $\delta^{18}\text{O}$ of quartz. Instead, the presence of H_2 and/or CH_4 might produce the observed variation (e.g., Wood et al., 1986; Kerrich, 1987). In fact, the latter has been detected, but only in small amounts, in the fluid inclusions. The $\delta^{13}\text{C}$ values of CO_2 recovered from fluid inclusions are somewhat variable. In the Caxias deposit, three samples have $\delta^{13}\text{C}$ values in the range of -5.3 and -10.9‰, and a fourth sample has a lower value

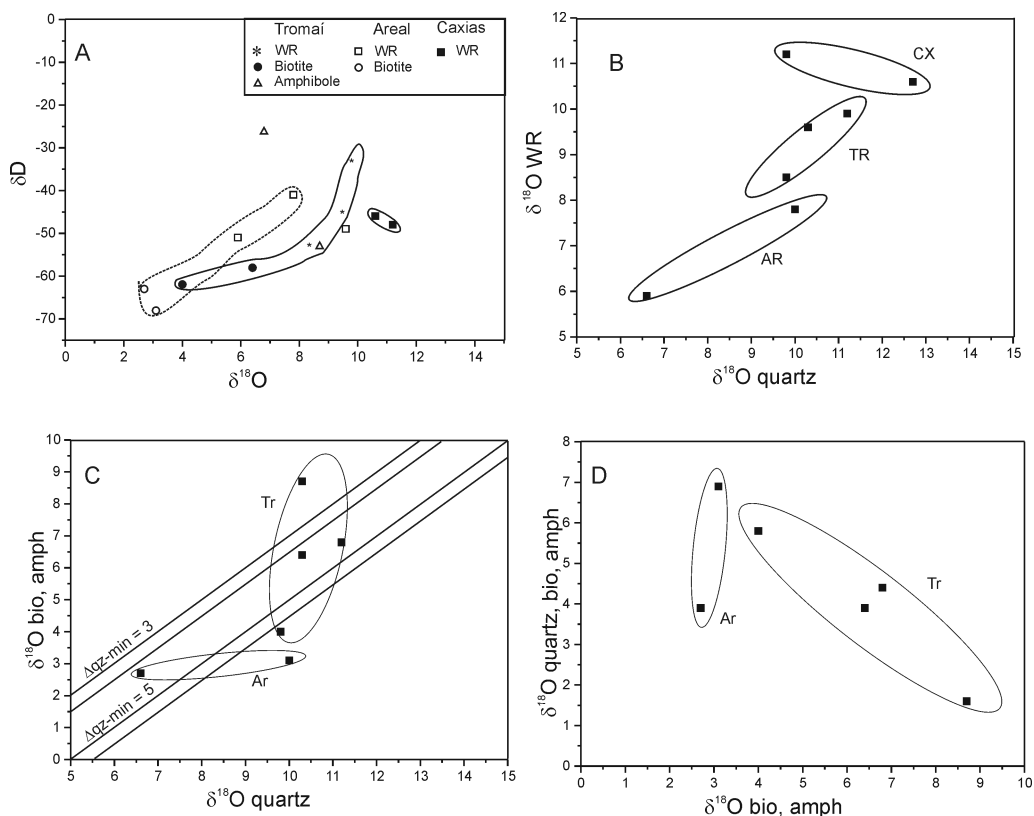


FIG. 3. Diagrams showing the stable isotope compositions and relationships of minerals and whole rocks from regional units of the São Luís crater. A and B. Distinct fields and trends for Tromaí, Areal, and Caxias units. C. Steep trend for the isotope compositions of the Tromaí unit, cutting across lines of magmatic equilibrium (solid lines). D. Negative slope for the isotope compositions of the Tromaí unit. Both B and D behaviors indicate re-equilibration at subsolidus temperatures (see text).

of -20.2‰ . At Areal and Pedra de Fogo, the $\delta^{13}\text{C}$ values of inclusion CO_2 is -8.9 and -3.1‰ , respectively. A single sample of calcite from the Caxias deposit shows $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of -9.1 and $+18.7\text{‰}$, respectively. Pyrite separates have $\delta^{34}\text{S}$ values of -11.0 , -0.5 , and -2.8‰ , respectively, in the Caxias, Areal, and Pedra de Fogo deposits.

Fluid composition and potential sources

The oxygen isotope composition of the fluid in equilibrium with quartz ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) was calculated from the isotopic ratios of the quartz and the quartz-water fractionation factor of Matsuhisa et al. (1979). The hydrogen isotope composition of the fluid ($\delta\text{D}_{\text{H}_2\text{O}}$) was measured directly in inclusion waters and estimated from the hydrous silicates δD values, using the mineral-water fractionation factor of

Graham et al. (1987) and the calibration of Bowers and Taylor (1985) for chlorite and muscovite, respectively. The $\delta^{13}\text{C}$ value of the CO_2 in the fluid comes from the isotope composition of the fluid inclusion CO_2 . The $\delta^{34}\text{S}$ values of the fluid were calculated from the $\delta^{34}\text{S}$ values of pyrite and the pyrite- H_2S fractionation factor of Ohmoto and Rye (1979), assuming H_2S as the main sulfur species in the fluid. For the calculations, temperatures determined from external geothermometers (fluid inclusion homogenization temperatures and chlorite chemical compositions) were used as follows: 262° to 307°C for Caxias; 260° to 300°C for Areal; and 330° to 400°C for Pedra de Fogo. The quartz-chlorite and quartz-muscovite oxygen isotope geothermometers (Zheng, 1993) were employed for the Caxias and Areal mineralizations, respectively, and only the quartz-muscovite pair from

TABLE 3. Stable Isotope Compositions of Hydrothermal Minerals of the Caxias, Areal, and Pedra de Fogo Gold Deposits

Sample	Host rock	Mineral	Host	Silicates		Carbonates		Fluid inclusions		Sulfides
				$\delta^{18}\text{O}$ (‰)	δD (‰)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	δD (‰)	$\delta^{34}\text{S}$ (‰)
					Caxias					
CX65	Microtonalite	Chlorite	Alter zone	+7.6	-46					
CX65	Microtonalite	Calcite	Alter zone			-9.1	+18.7			
CX65	Microtonalite	Pyrite	Alter zone							-11
CX65	Microtonalite	Quartz	Vein	+11.2				-10.9	-32	
CX11	Schist	Quartz	Vein	+11.3				-20.2	-53	
CX42A	Schist	Quartz	Vein	+11.0				-6.9	-24	
CX61D	Schist	Quartz	Vein	+12.2				-5.3	n.d. ¹	
					Areal					
AR4D	Monzogranite	Quartz	Vein	+10.4				-8.9	-62	
AR10C	Syenogranite	Sericite	Alter zone	+5.1	-58					
AR10C	Syenogranite	Pyrite	Alter zone							-0.5
					Pedra de Fogo					
PF10B	Pyroclastic	Quartz	Vein	+16.2				-3.1	-70	
PF1C	Metadacite	Pyrite	Alter zone							-2.8

¹n.d. — not determined.

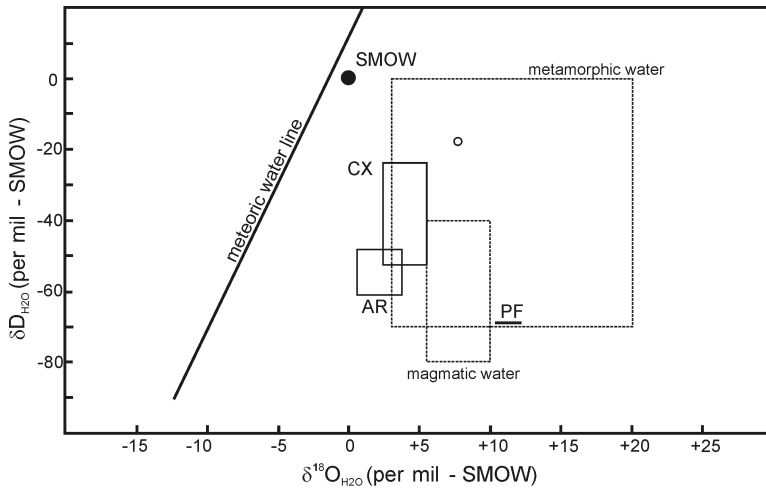


FIG. 4. $\delta^{18}\text{O}$ versus δD plot, showing the composition of the fluid in equilibrium with silicate minerals in the Caxias (CX), Areal (AR), and Pedra de Fogo (PF) gold deposits. The magmatic and metamorphic fields (dashed lines) were defined by Sheppard (1986).

Areal yielded a temperature value (273°C) in agreement with the previously determined formation temperatures.

The oxygen isotope composition of the fluid in the Caxias deposit ranges from $+2.6$ to $+5.6\%$. These results, combined with the δD values obtained in fluid inclusions, plot mostly in the field of metamorphic water (Fig. 4), as defined by Sheppard (1986). The chlorite sample (CX65) furnished a distinct value, which is more enriched in both $\delta^{18}\text{O}$ and δD than the range of values obtained from quartz and fluid inclusions. This can be attributed to retrograde isotopic exchange, or some compositional effect, such as the iron content of chlorite (e.g., Kyser, 1987). This value is, nevertheless, also consistent with a metamorphic origin (Fig. 4). At Areal, fluid $\delta^{18}\text{O}$ and δD vary between $+0.6/+3.5\%$ and $-49/-53\%$, respectively. These values are rather different from those of the Caxias deposit. They plot partially in the metamorphic field, but the oxygen isotope values are lower than the normal values accepted for metamorphic water (Fig. 4). Such low values have been interpreted as recording the involvement of isotopically evolved meteoric water in addition to metamorphic fluids (Kyser and Kerrich, 1990; Boiron et al., 2003). In fact, lower $\delta^{18}\text{O}$ values come from the sericite, which may undergo retrograde exchange (McCuaig and Kerrich, 1998). In the Pedra de Fogo occurrence, fluid $\delta^{18}\text{O}$ ranges from $+10.1$ to $+12.1\%$ and the $\delta\text{D}_{\text{H}_2\text{O}}$ is -70% .

These values are also consistent with a metamorphic origin for the fluids, which is in keeping with the fluid evolution proposed by Klein and Fuzikawa (2005) on the basis of fluid inclusion data. The higher $\delta^{18}\text{O}$ values may also reflect the presence of ^{18}O -enriched metasedimentary rocks in the fluid source reservoirs, as detected in Phanerozoic lode-gold deposits elsewhere (McCuaig and Kerrich, 1998, and references therein).

Among $\delta^{13}\text{C}$ values of the CO_2 measured in inclusion fluids and calculated from calcite analysis in the Caxias deposit, four values are in the range of -5.3 to -10.9% , and a fifth value is more negative, -20.2% . The latter reflects an organic source and is in accord with the occurrence of carbonaceous schists in the host rocks (Klein et al., 2000). The predominant values, as well as those determined in the Areal and Pedra de Fogo prospects, are considered to be normal for this type of deposit (e.g., McCuaig and Kerrich, 1998), but these values are not diagnostic of a single carbon reservoir, because mantle-, magmatic-, and metamorphic-derived carbon plots in this interval, and may also reflect mixing sources (Ohmoto, 1986; McCuaig and Kerrich, 1998). The concordance of the value obtained from calcite with those measured in the inclusion fluids indicates that calcite precipitated from the same CO_2 -bearing fluid trapped in the fluid inclusions.

The $\delta^{34}\text{S}$ value of the fluid is -12.2% at Caxias, -1.7% at Areal, and -3.8% in the Pedra de Fogo

prospect. These depleted values could have been produced by oxidation of the fluid through reaction with host rocks, but this is discounted based on absence of host rocks having oxidized phases, such as sulfates or hematite. The presence of small quantities of magnetite at Caxias, however, may suggest that the fluid attained locally more oxidized conditions. For deposits in the West African craton, having similar geologic and physicochemical characteristics, Oberthür et al. (1996) suggested syn-sedimentary-diagenetic sulfides present in the Birimian rocks as the most probable source for the sulfur in the gold deposits they studied.

Concluding Remarks

Available geological, petrologic, and geochronological information indicates that the major portion of the São Luis craton, which hosts the Caxias, Areal, and Pedra de Fogo gold deposits, records magmatic arc-/subduction-related environments as part of an accretionary orogen active in the Paleoproterozoic (2.2–2.1 Ga). The relative timing of gold mineralization was post-metamorphic and syn- to late-tectonic, with the deposits being controlled by minor shear zones and brittle structures. Previous chlorite and fluid inclusion studies showed that low-salinity aqueous-carbonic ($\pm\text{CH}_4\text{-N}_2$) fluids were responsible for the mineralization that occurred at 260°–300°C in the Caxias and Areal deposits, and at 330°–400°C in the Pedra de Fogo prospect, under average pressures of ~2 kbar, indicating depths of 6–7 km. Phase separation (immiscibility) and fluid-rock interactions were probably the main processes leading to gold deposition, possibly helped by oxidation and cooling of the fluid at Pedra de Fogo. Fluid mixing was not identified in any of the studied deposits.

The reconnaissance stable isotope study carried out on the two major suites of granitoids (Tromaf and Areal) of the São Luis craton and on samples of the Caxias Microtonalite and Aurizona Group reveal that the rocks probably were affected by minor subsolidus post-crystallization isotopic exchange. Granitoids of the Tromaf Intrusive Suite apparently were less affected than rocks of the three other units. It is noteworthy that samples of the Tromaf granitoids come from areas lacking known gold deposits. The determined isotope compositions probably reflect the regional metamorphism that affected the rocks from this unit. In turn, the three other units were sampled in areas of gold mineralization and wide-

spread hydrothermal alteration. These units show possible effects of lower temperature isotope exchange or re-equilibration, which could have been caused by hydrothermal alteration around the deposits.

The study of hydrothermal minerals associated with the Caxias, Areal, and Pedra de Fogo prospects reveals that the isotope composition of the ore-bearing fluids is consistent within deposits, showing variable differences between deposits. Oxygen and hydrogen isotopes show that metamorphic fluids were the main, if not unique, gold-transporting media (Fig. 3). In the case of the Areal prospect, lower $\delta^{18}\text{O}$ values of the fluid may be ascribed to evolved meteoric water. It is unlikely, however, that meteoric water was involved with the ore-bearing fluids. This would require mixing with the CO_2 -bearing metamorphic fluid, and this process has not been recognized. Infiltration of low-temperature and low-salinity aqueous fluids (consistent with a meteoric source) has been documented at Areal as a late process, unrelated to the mineralizing event (Klein et al., 2000). This may be the cause of the low $\delta^{18}\text{O}$ values. Carbon isotope results are not diagnostic of a specific source, being compatible with mantle, magmatic, metamorphic, or combined sources. One strongly negative $\delta^{13}\text{C}$ value reflects an organic influence. The negative values presented by the sulfur isotopes possibly record local oxidation of the ore-bearing fluids.

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